



PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Method of manufacturing Resinoids

We, HITACHI CHEMICAL COMPANY LTD., a Corporation organised under the laws of Japan, of 4, 1-chome, Marumouchi, Chiyodaku, Tokyo, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of manufacturing resinoids which are useful as coatings, impregnants, and laminated varnishes.

U.S. Patent Specifications Nos. 2,604,464, 2,662,870, and 2,798,861, describe thermo-setting resinoid compositions which are obtained by mixing copolymers of α,β unsaturated monocarboxylic acids and copolymerizable vinyl monomers with epoxy resins at room temperature.

The cured compositions, however, are formed only at high temperatures and after long cure periods, and moreover, the addition of curing catalysts may be necessary despite which the alkali and weather resistance of the compositions may be poor. The lack of compatibility of the components may also give rise to problems as the components are merely mixed physically. Use of high molecular weight epoxy resins such as "Epikote" 1001, "Epikote" 1004, and "Epikote" 1007 ("Epikote" is a registered Trade Mark) can limit both the type and the amount of the vinyl monomer used because of a lack of compatibility.

In addition, the selection of solvents is very

important for obtaining coating compositions with the best properties.

This invention provides thermo-settable resinoids which are stable at room temperature and can be cured quickly on heating. The cured resins have excellent physical properties such as toughness, and chemical-, stain-, solvent- and water-resistance.

In one aspect, the present invention provides a method of manufacturing resinoids by solution copolymerization, in the presence of 3—35 parts by weight of epoxide having an epoxy equivalent of 50—4,000 and a polymerization catalyst, of two different vinyl components, as hereinafter defined, in which the first vinyl component (1) is used in an amount of 4—40 parts by weight and is a mixture consisting of 2—20 parts by weight of α,β -unsaturated monocarboxylic acid and 2—20 parts by weight of one or more α,β -unsaturated monocarboxylic amide(s) and/or monoalkyl N-substituted derivative(s) thereof (wherein the alkyl group is of 1—4 carbon atoms), both ingredients of the mixture having functional group equivalents of 0.5—4.0 per epoxy equivalent, and the second vinyl component (2) is used in an amount of 30—80 parts by weight.

The resinoids thus obtained are high molecular weight graft copolymers possessing residual epoxy rings, amide, carboxyl and hydroxyl groups, and in some cases, imide groups as reacting functional groups. They can be cured quickly at comparatively low tem-

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peratures without the addition of curing catalysts. The epoxide becomes chemically combined with the vinyl compounds during formation of the copolymer and the physical compatibilities of the components of the copolymer become relatively important. Physical compatibility is important, however, in compositions such as those disclosed in the aforementioned U.S. Specifications where the components are merely mixed physically.

Even when high molecular weight epoxy resins are used in the method of this invention, a wide range of solvents can be used; for example, if "Epikote" 1001 is used the composition obtained is readily soluble in aromatic solvents, such as toluene and xylene, which are poor solvents for "Epikote" 1001 alone.

Diepoxides possessing polyether bonds are particularly suitable for use in the method of this invention. Condensation products of bisphenol-A and epichlorohydrin, for example, "Epikote" 828, "Epikote" 1001, "Epikote" 1004, "Epikote" 1007, and "Epikote" 1009, or "Araldite" 6071, "Araldite" 6084, "Araldite" 6097 and "Araldite" 6099 ("Araldite" is a registered Trade Mark) and condensation products of ethylene glycol and epichlorohydrin or of glycerine and epichlorohydrin may also be used. Other epoxy compounds that can also be used are, for example, epoxidized vegetable oils, the 3,4-epoxy-6-methylcyclohexylmethyl ester of 3,4-epoxy-6-methylcyclohexane carboxylic acid and the 3,4-epoxycyclohexylmethyl ester of 3,4-epoxycyclohexane carboxylic acid. Epoxides having an epoxy equivalent of 100-1000 are preferred. If more than 35 parts by weight of epoxide are used the stability of the resinoids and the weather resistance of the cured materials are lowered; further, the colour of the white enamel of the final product quickly changes to yellow, so the resinoid is not suitable for applications requiring high gloss retention and high yellowing resistance such as coatings for automobiles and domestic appliances.

Acrylic acid and methacrylic acid are examples of α,β -unsaturated monocarboxylic acids which are useful in this invention.

Useful unsubstituted and N-substituted α,β -unsaturated monocarboxylic amides include acrylamide and methacrylamide and N-methylacrylamide, N-ethylacrylamide, N-n-propylacrylamide, N-n-butylacrylamide, N-methylmethacrylamide, N-ethylmethacrylamide, N-n-propylmethacrylamide, and N-n-butylmethacrylamide.

Vinyl compounds suitable as component (2) include styrene, α -methylstyrene, vinyltoluene, acrylonitrile, methacrylonitrile, vinyl acetate, alkylvinyl ethers, alkyl acrylates wherein an alkyl group has 1-12 carbon atoms, such as methyl acrylate, ethyl acrylate, n-propyl acrylate, isopropyl acrylate, n-butyl acrylate, isobutyl acrylate, tert.-butyl acrylate and 2-

ethylhexyl acrylate, and alkyl methacrylates wherein an alkyl group has 1-12 carbon atoms, such as methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, butyl methacrylate, isobutyl methacrylate, tert.-butyl methacrylate and 2-ethyl hexyl methacrylate. "Vinyl compounds" as used herein means compounds containing the group $\text{CH}_2=\text{C}<$.

One or more of these vinyl compounds may be used as component (2) but it should be understood that the vinyl compounds which can be used as component (2) do not include the monocarboxylic acids, amides or N-alkyl amides which are used in component (1).

According to this invention, solution copolymerization of components (1) and (2) is carried out in the presence of a copolymerization catalyst such as an organic peroxide, e.g. benzoyl peroxide, di-tert.-butylperoxide, and cumene hydroperoxide, or azo compound, e.g. α,α' -azobisisobutyronitrile, in the presence of the epoxide.

The solvent used in the solution copolymerization may be, for example, an alcohol, toluene, xylene, methylethylketone, butyl-Cellosolve ("Cellosolve" is a registered Trade Mark), dioxane, a toluene-butanol mixture, or a xylene-n-butanol mixture. Preferably solution copolymerization is carried out with 0.5-3.0% by weight of catalyst, based on the vinyl component (2), at 70°-130° C. for 0.5-7.0 hours.

As described above, the resinoids prepared in accordance with this invention can be useful coatings by themselves; however, if suitable alkyletherified amino resins or alkyletherified phenol resins or mixtures thereof are added to the resinoids of the invention curing at lower temperatures (110°-150° C.) becomes possible, and improved physical and chemical properties result. Alkyletherified amino resins include condensation products of aldehydes, such as formaldehyde or paraformaldehyde with amino compounds such as urea, N,N'-ethylene urea, dicyandiamide or aminotriazine alkyletherified with alcohols having 1-6 carbon atoms; examples of such alkyletherified condensation products are methylated methylolurea, methylated methylol-N,N'-ethylene urea, methylated methyloldicyandiamide, methylated methylolmelamine, methylated methylolbenzoguanamine, butylated methylol-N,N'-ethylene urea, butylated methyloldicyandiamide, butylated methylolmelamine, butylated methylolbenzoguanamine; alkyletherified phenol resins include condensation products of aldehydes, such as formaldehyde or paraaldehyde with phenols or their derivatives, such as, for example, alkylphenols such as *para*-octylphenol, *para*-tert. butylphenol, and *para*-cyclohexylphenol, and phenols such as *ortho*-cresol, *para*-cresol, xlenol and bisphenol-A, alkyletherified with alcohols having 1-6 carbon atoms; examples

of alkyletherified condensation products of this form are, for example, butylated methylol-*para*-octylphenol, butylated methylol-*para*-tert. butylphenol, butylated methylol-*para*-cyclohexylphenol, butylated methylolbisphenol-A, butylated methylol-*ortho*-cresol, butylated methylol-*meta*-cresol, and butylated methylol-*para*-cresol. These alkyletherified amino resins or alkyletherified phenol resins are preferably added in the amount of 5—50, especially 15—25, parts by weight to 95—50, especially 85—75, parts by weight of the resinoid obtained according to this invention.

Though it is possible, within the range of compatibility, to add more than 50 parts by weight of alkyletherified resins to 50—95 parts by weight of the resinoids, the only advantage is increased hardness of the cured products; their toughness, flexibility, adhesive properties, impact strength, and waterproofing properties tend to be decreased. In general alkyletherified amino resins impart hardness, toughness, high impact strength, strain resistance, and low temperature curing and waterproofing ability while alkyletherified phenol resins impart chemical resistance, waterproofing properties, and flexibility.

The invention is illustrated by the following Examples and Reference Example, in which parts are by weight.

REFERENCE EXAMPLE.

23.8 parts of styrene, 34 parts of ethyl acrylate, 3.0 parts of methacrylic acid, 5.4 parts of acrylamide, and, as solvents, 35 parts of xylene and 15 parts of n-butanol are weighed, put in a flask equipped with an agitator, a thermometer, a reflux condenser, a dropping funnel and a gas inlet tube, and the flask is heated to 80°C. 13.7 parts of styrene, 16.8 parts of ethyl acrylate, 3.3 parts of methacrylic acid, and as catalyst, a mixture of 0.9 parts of α,α' -azobisisobutyronitrile and 0.6 parts of di-tert.-butylperoxide are added dropwise over 30 minutes. The reaction is continued for 30 minutes at 80°C. and for a further 5 hours at 110°C. The product is then diluted with 46.3 parts of xylene and 3.7 parts of n-butanol, and 20 parts of a solution prepared by dissolving 10 parts of "Epikote" 1001 in 5 parts of xylene and 5 parts of n-butanol are mixed with 80 parts of the copolymer solution.

EXAMPLE 1.

20 parts of "Epikote" 1001, 18.8 parts of styrene, 28.5 parts of ethyl acrylate, 2.4 parts of methacrylic acid, 4.3 parts of acrylamide, and as solvents, 25 parts of xylene and 25 parts of n-butanol are weighed and put in the same flask as used in the Reference Example.

The flask is heated to 80°C., and 11.2 parts of styrene, 11.8 parts of ethyl acrylate, 2.6 parts of methacrylic acid, and as cata-

lyst, a mixture of 0.9 parts of α,α' -azobisisobutyronitrile and 0.6 parts of di-tert.-butylperoxide are added dropwise over 30 minutes, and the flask is kept at 80°C. for 30 minutes; the reaction is then allowed to continue for 5 hours at 110°C. The reaction product is diluted with 50 parts of xylene and a copolymer solution having a non-volatile content of 50%, a viscosity of W—X (Gardner viscosity index), an acid value of 15.6 and a colour number of less than 1 (Gardner) is obtained.

The compositions obtained in the Reference Example and Example 1 have the same composition. However, while the solution of the Reference Example is also opaque that of Example 1 is transparent; and on making a film from each of them at room temperature, the former is turbid and opaque, while the latter is transparent. On heating, the former produces an opaque coating composition of little value, whereas the latter produces a transparent and therefore valuable coating composition. The toluene tolerance at 20°C. of the latter is 1.8 times that of the former. The thermosetting resin prepared from the resinoid according to this invention is therefore quite different from the thermosetting resin prepared conventionally. Moreover, as the resinoids prepared according to this invention are not merely physical mixtures, they show an excellent spray coating workability.

EXAMPLE 2.

20 parts of "Epikote" 1001, 18.8 parts of methyl methacrylate, 28.5 parts of ethyl acrylate, 2.4 parts of methacrylic acid, 4.3 parts of acrylamide, and as solvents, 25 parts of xylene and 25 parts of n-butanol are weighed and put in the same flask as used in the Reference Example. This is heated to 80°C., and 11.2 parts of methyl methacrylate, 11.8 parts of ethyl acrylate, 2.6 parts of methacrylic acid, and as catalyst, a solution mixture consisting of 0.9 parts of α,α' -azobisisobutyronitrile and 0.6 parts of di-tert.-butylperoxide are added dropwise over 30 minutes. The reaction is kept for 30 minutes at 80°C., and then is continued for 5 hours at 110°C. The product is then diluted with 50 parts of xylene and a copolymer solution having a non-volatile content of 50.1%, a viscosity of Y—Z, an acid value of 15.3, and a colour number of less than 1 is obtained.

EXAMPLE 3.

30 parts of "Epikote" 1001, 18.8 parts of vinyl toluene, 28.5 parts of n-butyl acrylate, 2.4 parts of acrylic acid, 4.3 parts of acrylamide, and as solvents, 25 parts of xylene and 25 parts of n-butanol are weighed and put in the same flask as used in the Reference Example. This is heated to 80°C., and 11.2 parts of vinyl toluene, 11.8 parts of n-butyl

acrylate, 2.6 parts of methacrylic acid, and as catalyst, a solution mixture consisting of 0.9 parts of α,α' -azobisisobutyronitrile and 0.6 parts of di-tert.-butylperoxide are added dropwise over 30 minutes. The reaction is kept for 30 minutes at 80° C. and then is continued for 5 hours at 110° C. The product is diluted with 50 parts of xylene. The copolymer solution obtained possesses a non-volatile content

of 49.5%, a viscosity of W, an acid value of 15.7 and a colour number of less than 1.

100 parts of the epoxy modified copolymer solution obtained in Examples 1—34 are each converted into white enamel with 50 parts of rutile-type titanium dioxide, and each is baked on steel plates at 170° C. for 30 minutes; Table 1 shows some of their properties.

TABLE 1

Specimen		Example 1	Example 2	Example 3
Item				
Gloss		95	99	98
Degree of yellowness		-4.952	-3.244	-5.245
Clemens scratch Hardness		158	198	165
Adhesive property	Crosscut	Excellent	Excellent	Excellent
	Sketch	Excellent	Excellent	Excellent
	Erichsen (mm)	8.7	5.0	8.8
	Impact (cm)	50	45	More than 50
Flexibility (Φ)		3	3	3
Chemical resistance	5% NaOH aqueous solution	Unchanged	Unchanged	Unchanged
	5% HCl aqueous solution	Unchanged	Unchanged	Unchanged
	5% neutral detergent	Unchanged	Unchanged	Unchanged
Boiling water resistance		Unchanged	Unchanged	Unchanged
Stain resistance	Red ink	Unchanged	Unchanged	Unchanged
	Blue ink	Unchanged	Unchanged	Unchanged
	Mustard	Unchanged	Unchanged	Unchanged
Coating workability		Excellent	Good	Excellent

20 In Table 1, gloss is measured with a Hunter gloss meter; degree of yellowness is represented by $Y = \frac{A-B}{G} \times 100$; impact

strength is measured with a du Pont impact tester having $\frac{1}{2}$ in. diameter and 1 kg load; 25 chemical resistance is observed by immersing specimens in each chemical for 3 hours at 70° C; boiling water resistance is observed by immersing specimens in boiling water for 2 hours at 100° C.; stain resistance is observed by coating with each material for 24 30 hours at the normal room temperature. The

similar tests in other Tables throughout this specification are performed by the same methods, unless otherwise stated.

EXAMPLE 4.

A composition (with a non-volatile content of 50%) is obtained by mixing 70 parts of the resinoid prepared in Example 1 with 30 parts of butylated methylolmelamine.

It is made into white enamel by adding rutile-type titanium dioxide, and baked on a steel plate at 130° C. for 30 minutes. A coating film with properties as shown in Table 2 is obtained.

EXAMPLE 5.

85 parts of the resinoid obtained in Example 1 are mixed with 5 parts of butylated methylol urea and 10 parts of butylated methylolmelamine to give a product which is made into white enamel, as described in Example 4, and baked on a steel plate at 150° C. for 30 minutes. The properties of the coating film so obtained are shown in Table 2.

EXAMPLE 6.

70 parts of the resinoid obtained in Example 2 are mixed with 30 parts of methylated methylolbenzguanamine to give a product

which is made into white enamel, as described in Example 4, and baked on a steel plate at 150° C. for 30 minutes. The properties of the coating film so obtained are shown in Table 2.

EXAMPLE 7.

70 parts of the resinoid obtained in Example 3 are mixed with 30 parts of butylated methylolmelamine, and the product is made to white enamel, as described in Example 4, and baked on a steel plate at 130° C. for 30 minutes. The properties of the coating film so obtained are shown in Table 2.

TABLE 2

Specimen		Example 4	Example 5	Example 6	Example 7
Item					
Gloss		98	99	98	97
Degree of yellowness		-7.042	-6.093	-7.532	-6.987
Clemon's scratch hardness		155	152	150	148
Adhesive property	Crosscut	Excellent	Excellent	Excellent	Excellent
	Sketch	Excellent	Excellent	Excellent	Excellent
	Erichsen (mm)	5.8	5.2	6.7	7.8
	Impact (cm)	35	30	35	45
Flexibility (Φ)		3	3	3	3
Boiling water resistance		Unchanged	Unchanged	Unchanged	Unchanged
Gasoline resistance		Unchanged	Unchanged	Unchanged	Unchanged
Chemical resistance	5% NaOH aqueous solution	Unchanged	Unchanged	Unchanged	Unchanged
	5% HCl aqueous solution	Unchanged	Unchanged	Unchanged	Unchanged
Stain resistance	5% neutral detergent solution	Unchanged	Unchanged	Unchanged	Unchanged
	Red ink	Unchanged	Unchanged	Unchanged	Unchanged
	Blue ink	Unchanged	Unchanged	Unchanged	Unchanged
	Mustard	Unchanged	Unchanged	Unchanged	Unchanged
Coating workability		Excellent	Excellent	Good	Excellent

EXAMPLE 8.

After blending 90 parts of the resinoid obtained in Example 1 with 10 parts of butylated methylolalkylphenol resin (the

alkylphenol being bisphenol-A), the mixture is flowed to coat a steel plate and baked at 170° C. for 30 minutes.

EXAMPLE 9.

70 parts of the resinoid obtained in Example 1 are mixed with 30 parts of butylated methylolalkylphenol resin (the alkylphenol being *para*-tert.-butylphenol), and the mixture is baked on a steel plate under the same conditions as in Example 8.

EXAMPLE 10.

A mixture of 90 parts of the resinoid obtained in Example 2 with 10 parts of butylated methylolalkylphenol resin (the alkylphenol

being *meta*-cresol) is baked on a steel plate under the same conditions as in Example 8.

EXAMPLE 11.

A mixture of 90 parts of the resinoid obtained in Example 2 with 10 parts of butylated methylolalkylphenol resin (the alkylphenol being bisphenol-A) is baked on a steel plate under the same conditions as in Example 8.

The properties of coating films baked according to Examples 8—11 are shown in Table 3.

TABLE 3

Specimen Item		Example 8	Example 9	Example 10	Example 11
Degree of yellowing		Light Yellow	Yellow	Light Yellow	Light Yellow
Sward rocker value		30	32	31	28
Adhesive property	Crosscut	Excellent	Excellent	Excellent	Excellent
	Sketch	Excellent	Excellent	Excellent	Excellent
	Erichsen (mm)	8.6	7.7	8.0	8.8<
	Impact (cm)	35	30	40	50
Flexibility (Φ)		0	0	0	0
Boiling water resistance		Unchanged	Unchanged	Unchanged	Unchanged
Chemical resistance	5% NaOH aqueous solution	Unchanged	Unchanged	Unchanged	Unchanged
	5% H ₂ SO ₄ aqueous solution	Unchanged	Unchanged	Unchanged	Unchanged
	5% neutral detergent solution	Unchanged	Unchanged	Unchanged	Unchanged

In Table 3, hot water resistance is observed by immersing the film in boiling water for 4 hours; chemical resistance is observed by immersing it in each chemical for 5 hours; the testing methods in Table 4 are the same as in Table 3.

EXAMPLE 12.

A mixture of 75 parts of the resinoid obtained in Example 1 with 10 parts of butylated methylolmelamine and 15 parts of butylated methylolbisphenol-A is baked on a steel plate under the same conditions as in Example 8.

EXAMPLE 13.

5 parts of butylated methylolbenzguanamine and 25 parts of butylated methylolbis-

phenol-A are added to 70 parts of the resinoid obtained in Example 2 and mixed, and the mixture is baked on a steel plate under the same conditions as in Example 8.

EXAMPLE 14.

10 parts of butylated methylolurea and 10 parts of butylated methylol *para*-cresol are added to 80 parts of the resinoid obtained in Example 3 and mixed, and the mixture is baked on a steel plate under the same conditions as in Example 8.

The properties of coating films obtained in Example 12—14 are shown in Table 4.

TABLE 4

Specimen		Example 12	Example 13	Example 14
Item				
Degree of yellowing		Light yellow	Light yellow	Pale yellow
Sward rocker value		32	39	34
Adhesive property	Crosscut	Excellent	Excellent	Excellent
	Sketch	Excellent	Excellent	Excellent
	Erichsen (mm)	8.2	7.9	8.0
	Impact (cm)	40	35	45
Flexibility (Φ)		0	0	0
Boiling water resistance		Unchanged	Unchanged	Unchanged
Chemical resistance	5% NaOH aqueous solution	Unchanged	Unchanged	Unchanged
	5% H ₂ SO ₄ aqueous solution	Unchanged	Unchanged	Unchanged
	5% neutral detergent solution	Unchanged	Unchanged	Unchanged

Although the resinoids prepared according to this invention are very stable, they may be cured quickly by heating to a low temperature without curing catalysts. The cured materials show excellent properties as can be seen from the previous Tables.

WHAT WE CLAIM IS:—

1. A method of manufacturing resinoids by solution copolymerization, in the presence of 3—35 parts by weight of epoxide having an epoxy equivalent of 50—4,000 and a polymerization catalyst, of two different vinyl components, as hereinbefore defined, in which the first vinyl component (1) is used in an amount of 4—40 parts by weight and is a mixture consisting of 2—20 parts by weight of α,β -unsaturated monocarboxylic acid and 2—20 parts by weight of one or more α,β -unsaturated monocarboxylic amide(s) and/or monoalkyl N-substituted derivative(s) thereof (wherein the alkyl group is of 1—4 carbon atoms), both ingredients of the mixture having functional group equivalents of 0.5—4.0 per epoxy equivalent, and the second vinyl component (2) is used in an amount of 30—80 parts by weight.

2. A method according to claim 1 in which there is used an epoxide having an epoxy equivalent of 100—1000.

3. A method according to claim 1 or 2 in which the polymerization catalyst is an organic peroxide or an azo compound.

4. A method according to any preceding claim in which the copolymerization is carried out with 0.5—3.0% by weight of catalyst, based on the weight of the vinyl component (2), at 70°—130° C. for 0.5—7 hours.

5. A method according to claim 1, substantially as hereinbefore described.

6. Resinoids when manufactured by the method claimed in any one of claims 1—5.

7. Compositions comprising a resinoid as claimed in claim 6 and an alkyletherified amino resin or an alkyletherified phenol resin or a mixture thereof.

8. Compositions according to claim 7 in which the alkyletherified amino resin is a condensation product of an aldehyde with an amino compound alkyletherified by an alcohol of 1—6 carbon atoms.

9. Compositions according to claim 7 in which the alkyletherified phenol resin is a condensation product of an aldehyde with a phenol alkyletherified by an alcohol of 1—6 carbon atoms.

10. Compositions according to any of claims 7—9 which comprise 5—50 parts by weight of alkyletherified resin and 50—95 parts by weight of resinoid.

11. Compositions according to claim 10 which comprise 15—25 parts by weight of alkyletherified resin.

12. Resinoids according to claim 6, substantially as described in any of Examples 1—3.

13. Compositions according to claim 7, sub-

stantially as described in any of Examples
4—14.

14. Resins formed by curing resinoids
claimed in claim 6 or 12 or a composition
5 claimed in any of claims 7 to 11 and 13.

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Fig. 1.

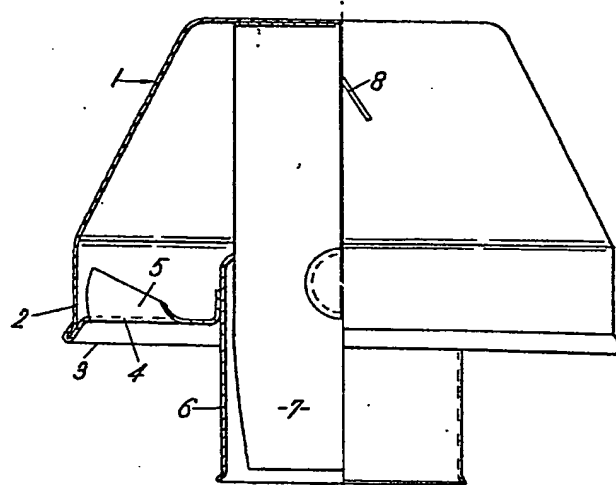


Fig 2

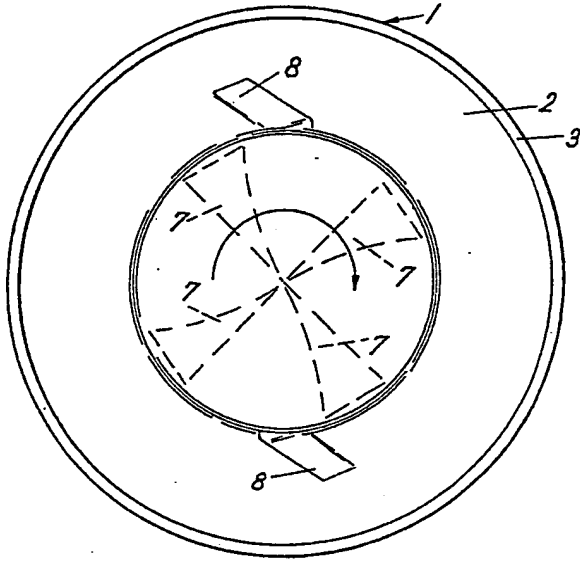
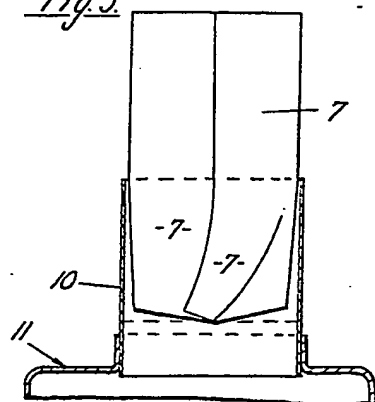


Fig 3



1073907 COMPLETE SPECIFICATION
 2 SHEETS This drawing is a reproduction of
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 Sheets 1 & 2

